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Request for grant of a patent

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2	Patent application number	9904289.7
3	Full name, address and postcode of the applicant Patents ADP number State of incorporation	British Nuclear Fuels plc Risley WARRINGTON WA3 6AS 35010800 1 UK
4	Title of the invention	Analytical Instrument
5	Name of agent Address for service Patents ADP number	Harrison Goddard Foote Belmont House 20 Wood Lane Headingley Leeds LS6 2AE 14571001

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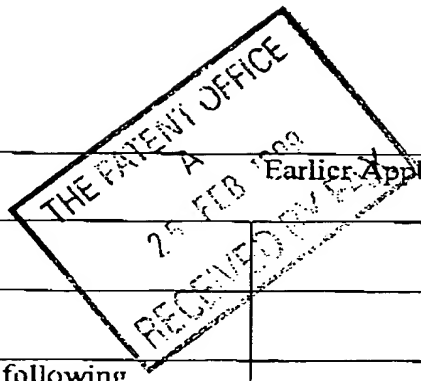

7	Parent application (eg Divisional)	Earlier Application No	Date of Filing
8	Statement of Inventorship Needed?		
9	Number of sheets for any of the following (not counting copies of same document)		
	Continuation sheets of this form		
	Description	9	
	Claims	4	
	Abstract		
	Drawings	2	
10	Number of other documents attached		
	Priority documents		
	Translations of priority documents		
	P7/77		
	P9/77	1	
	P10/77		
	Other documents		
11	I/We request the grant of a patent on the basis of this application.		
	Signature S.P. Gilholm	Date 25 Feb 1999	
12	Name and daytime telephone number of person to contact in the United Kingdom	STEVE GILHOLM +44 113 2258350	

ANALYTICAL INSTRUMENT

This invention relates to a novel analytical instrument, and to novel methods of measuring, *inter alia*, low concentrations of stable and radioisotopes and/or low abundance isotopes.

The determination of radionuclides at environmental levels using classical radiometric counting is well established and likely to remain the method of choice for short half-life species. However, innovations in analytical instrumentation in the last ten years have the potential to replace radiometric counting for a wide range of longer half-life species.

Elemental and isotopic analysis has advanced significantly with the introduction of plasma source mass spectrometry. A variety of plasmas have been used as ionization sources, e.g., glow discharges, microwave induced plasmas, but the inductively coupled plasma (ICP) is the most widely accepted, and *de facto*, the preferred ion source for atomic mass spectrometry. The inductively coupled plasma is compatible with solid, liquid or gaseous sample introduction and is a robust and efficient ionization source for atomic mass spectrometry.

For some potential applications of plasma mass source spectrometry, *e.g.*, environmental and biomedical monitoring of radioisotopes, current techniques may not possess the required sensitivity or selectivity. Classical radiometric techniques provide the required sensitivity, but do so at the expense of protracted count times and extensive sample preparation and clean-up. For example, within a plutonium bioassay program, current radiometric methods offer detection limits of 500 μBq per litre, but require 1-2 days of sample preparation and radiometric count times of, *e.g.*, four days with -spectrometry and up to 28 days for -track counting. There is therefore a requirement to develop plasma source mass spectrometry to provide enhanced selectivity and sensitivity without sacrificing the inherent flexibility, rapidity and robustness of the technique.

The instrument of the invention is designed to measure isotopes at extremely low concentrations and isotopes of very low abundance. An example of this would be the ultra low level determination of the radionuclides. The increasing interest in the behaviour of radionuclides in the biosphere requires that new methods be developed that have sensitivity equivalent to, or better than, that of the existing techniques, but combine this with superior speed and a reduced cost of analysis. Improvements in speed are essential to enable wider screening, plant and event management and to monitor illicit uses of nuclear materials. The recent OSPAR agreement has committed the UK to real reductions in levels of liquid effluent discharges. For many radionuclides, conventional radiochemical analysis will limit the ability to demonstrate that such reductions have been achieved.

To achieve the aim of improved detection limits in plasma source mass spectrometry, the factors that limit the selectivity and sensitivity of inductively coupled plasma mass spectrometry (ICP-MS) were considered. The instrumental detection limits available from ICP-MS are, in most cases, limited by the background count and not the magnitude of the analytical signal derived from the ions of interest. The background is derived broadly from three distinct sources:

1. A non-specific instrumental background.

2. Interferences from atomic or molecular ions of the same nominal mass to charge ratio, consequent upon insufficient mass spectral resolution. Examples of these "isobaric" interferences include atomic ions such as; $^{241}Am^{+}$, $^{241}Pu^{+}$; $^{90}Sr^{+}$, $^{90}Zr^{+}$; $^{55}Fe^{+}$, $^{55}Mn^{+}$; ^{40}Ca, ^{40}Ar; $^{204}Pb^{+}$, $^{204}Hg^{+}$ or molecular ions such as $^{238}U^{1}H^{+}$, $^{239}Pu^{+}$; $^{40}Ar^{16}O^{+}$, $^{56}Fe^{+}$,$^{40}Ar^{35}Cl^{+}$, $^{75}As^{+}$

3. Isotopes of different nominal masses but present at high relative abundances, consequent upon insufficient abundance sensitivity. For example, ^{88}Sr; ^{84}Sr, ^{90}Sr; $^{55}Fe^{+}$, $^{56}Fe^{+}$.

These observations are the key to development of instrumentation with the superior detection limits required for determination of radionuclides at background environmental and biomedical concentrations by ICP-MS techniques.

A comparison of alternative techniques to plasma source mass spectrometry suggests that resonance ionisation mass spectrometry (RIMS) offers similar or better absolute detection limits than achieved with current generation ICP-MS instruments, *e.g.* about 4 x 10^6 atoms for ^{239}Pu. The singular advantage of RIMS over, for example, ICP-MS, is the greater isotopic selectivity derived from the laser induced ionisation process. However, the prior chemical separation, though less demanding than that required by radio-chemical methods, is nevertheless time consuming and requires specific recovery of the element, deposition onto a Ta foil and overplating with Ti. Accelerator mass spectrometry (AMS) offers absolute detection power of the order of 10^6 atoms. Selectivity is achieved through the use of high energy dissociation of molecular ions and avoidance of isobars through negative ion discrimination. Improved detection limits are obtained by high energy counting to discriminate against detector background. High abundance sensitivity is achieved by acceleration to high potentials thus minimizing the relative ion energy spread. However, AMS involves large, complex and costly instrumentation. Sample preparation is complex and time consuming, requiring preparation of the element in a pure form. For these reasons, AMS is restricted to highly specialized roles and cannot be considered as a laboratory scale or general purpose instrument.

Thus, we have now developed an analytical instrument and an analytical approach that overcomes or mitigates the problems with conventionally known instruments and techniques. As a technology demonstration, this new device is based upon an ICP-MS instrument, but is equally applicable to other forms of plasma mass

spectrometry. Indeed, the range of applications includes all forms of atomic mass spectrometry and molecular mass spectrometry. This instrumentation also provides a flexible platform for spectroscopic studies of atoms and molecules to determine fundamental parameters.

Thus according to the invention, we provide an instrument comprising of a Plasma Source Mass Spectrometer equipped with dual ion detectors.

The instrument of the invention is preferably an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-MS instrument of the invention is adapted to operate in a multi-dimensional detection mode.

The instrument is provided preferably with detectors which are based upon specific detection of transmitted ions, *e.g. via.* optical spectroscopy. The device is in principle, an ICP-MS instrument operating in a multi-dimensional detection mode and including the following:

- A conventional non-specific ion detection device.
- A device based upon optical spectroscopy to provide highly selective and specific detection of ions transmitted by the mass spectrometer.

The detector device based upon optical spectroscopy provides:

- A high resolution detection system, which in conjunction with conventional mass spectrometry, is capable of resolving ions of interest from interfering molecular ions of similar nominal mass to charge ratio.
- A high resolution spectroscopy system, which in conjunction with conventional mass spectrometry, is capable of resolving ions of interest from atomic ions of similar nominal mass to charge ratio.

- A high resolution spectroscopy system, which in conjunction with conventional mass spectrometry, provides very high abundance sensitivity.

Operation of the two detection systems as a single integrated coincidence detector that provides:

- Background count rates that are orders of magnitude lower than those obtained if the individual detection systems were used as isolated, individual detectors.

The descriptive term for this approach is Inductively Coupled Plasma Mass Spectrometry Coincidence Laser Spectroscopy (ICP-MS-CLS).

Thus, according to a preferred feature of the invention, we provide an ICP- MS-CLS instrument. We especially provide an ICP-MS-CLS instrument with a conventional non-specific ion detection device and a device based on optical spectroscopy as hereinbefore defined.

The instrument of the invention supplements the universal ion counting detector with one that has a high degree of species selectivity. The use of a detector based on resonance scattering from the ions to be detected, *e.g.*, laser induced fluorescence (LIF), provides vastly improved selectivity thereby removing the problem of isobaric interferences derived from either atomic or molecular ions. Additionally, by operating the optical detector in time correlation with a second detector, background count rates can be reduced by several orders of magnitude.

The instrumentation takes advantage of improved detector technology to achieve very high spatial and temporal resolution in the optical spectroscopy. This allows coincidence detection from single photons. This capability is important in that it allows the detection of ions in which there is a high probability of trapping in a

metastable state. Ions in metastable states are transparent to the exciting laser and thus the overall photon multiplicity from these ions is low.

To allow for efficient interaction between the laser and ion beam, the ion beam must be defined accurately in space and be focussed to approximately the beam diameter of the laser. An imaging spectrometer provides an ideal solution and a sector mass spectrometer is one such device. A commercial, double focussing, sector ICP-MS provides the basic platform for development of ICP-MS-CLS.

A key feature of this instrument is the manipulation of the ion energies. To couple efficiently the energy from the laser into the ion to be detected, the optical bandwidths have to be matched. For example, an ion beam of energy of 5000 ± 2.5 eV, has a Doppler spread of about 100 MHz for an ion of mass = 240. This is in excess of the natural line width which is off the order of 15 MHz. The ion energies were manipulated by two devices. The first involves the introduction of a collision/reaction cell to act as an ion bridge between the sampler/skimmer plasma interface and the mass spectrometer. This thermalises the ions and reduces their energy spread to less than 1 eV. Additionally, it enables selective gas phase chemistry to dissociate interfering molecular ions. The second method involves acceleration of the ions to compress the optical bandwidth of the ions to be detected. For example, an ion beam of mass 240 but with a 40 000 ± 5 eV energy range has a corresponding Doppler spread of about 37 MHz. In practice, by using a collision/reaction cell, lower standing voltages, *e.g.*, 10kV, can be employed. Assuming an ion energy spread of, *e.g.*, 1 eV, at 10 kV, the Doppler spread is about 15 MHz which approximates natural line widths.

Programmed acceleration of the ions within the optical detector is important and ensures that the ions to be detected come into resonance with the exciting laser within the detection volume of the optical detector. This prevents optical trapping of the ions prior to their arrival in the detection volume of the optical detector.

The abundance sensitivity of the spectrometer can be improved by three methods:

- Where the analyte exhibits an isotope shift, the ion of interest can be brought into resonance selectively.
- Selective excitation of one hyperfine branch of an ion of interest can also be used to increase the selectivity of the mass spectrometer.
- Many ions do not exhibit an isotope shift that can be resolved optically, but acceleration of the ions induces an isotope shift by Doppler shifting the resonant frequency of the low abundant ion away from the interfering major isotope.

Many useful CLS transitions have been identified for neutral atoms and these the occur in the visible part of the spectrum. This has the advantage that the visible region of the spectrum is more readily accessible by tuneable lasers. Provision may be made for a charge exchange cell to be added to the flight tube to neutralise ions if required.

Where optical trapping of the ions of interest becomes significant, this may be addressed *via* the use of two-colour excitation schemes in which the metastable state is in resonance with one of the laser frequencies. To provide maximum flexibility and elemental coverage, a two-colour CW laser system was employed. A twin laser system allows a variety of excitation schemes to be used, combining single color, two color, multiphoton excitation and combinations thereof.

A multi-slit assembly was included in the instrumentation for simultaneous detection of major isotopes, to be monitored via conventional detectors, to allow isotope ratio measurements. This will also provides reference beams so that the performance of the sample introduction system and ICP ion source can be monitored continuously and optimized.

The invention will now be illustrated, but in no way limited, with reference to the following examples and the accompanying drawings, in which,

figure 1 is a schematic representation of a Coincidence Laser Spectrometer, and

figure 2 is a schematic representation of a multi-detector head including a detector based upon a Coincidence Laser Spectrometer.

Referring to figure 1, a coincidence laser spectrometer (1) comprises an optical detector (2) coupled to a voltage programmer flight tube (3), which tube is provided with a laser system (4) and a non-specific ion detector (D1). Charged beam steering plates (5) are situated adjacent to an exit port from the flight tube. The apparatus may be provided with beam dumping means (6) adjacent to spectrometer exit slits (7).

Referring to figure 2, a spectrometer assembly (8) comprises a multi-slit assembly (9) coupled to conventional ion-detectors (10 and 11) and a coincidence laser spectrometer (12) (as defined by figure 1).

Example 1

Verification of Instrument Performance – Determination of Low Abundance Isotopes, e.g. ^{10}Be

The operating characteristics of the system were established *via* an established CLS transition, *e.g.*, the Be (II) line at 313 nm which is readily accessible to a CW tunable laser. Beryllium is an important element in its own right and its high mass isotope (^{10}Be) is an important geochronometer. It is produced by nuclear spallation of oxygen by cosmic rays and reaches an equilibrium concentration in surface quartz of about 2 x 10^7 atoms per g^{-1}. An isobaric interference with ^{10}B exists, but this can be resolved in the optical detector. A reasonable measurement of ^{10}Be was made by processing of a 5g solution after removal of the major matrix elements. Other cosmogenic isotopes that might be amenable to detection include those of K, Cs, Ca, Mn, Ni, Pd, Al and the lanthanides depending on identifying suitable spectroscopic transitions.

Example 2

Determination of Pu in Urine for Bioassay Purposes.

An aliquot of urine was spiked with a Pu tracer, processed to remove the bulk of the matrix and yielded a final sample volume of 1 cm^3. This sample was analyzed by ICP-MS-CLS using a low flow sample introduction system. The isotope ratios of ^{238}Pu, ^{239}Pu, ^{240}Pu with respect to the tracer isotope were estimated. The tracer isotope was monitored on a conventional detector whilst the isotopes of interest were determined using CLS detection. Isobaric interferences from, for example, $^{238}U^+$, $^{238}U^1H^+$, $^{204}Pb^{35}Cl^+$, ^{241}Am, were resolved optically in the CLS detector. A complete chemical separation of Pu from the matrix was not required and a simple, rapid, group separation of the actinides yielded a sample suitable for analysis by ICP-MS-CLS.

Example 3

Determination of Fundamental Nuclear Parameters

Optical isotope shifts and fine structure can be used to probe nuclei for the purpose of deriving fundamental nuclear data. The ICP-MS-CLS instrumentation allows the precise measurement of optical isotope shifts using the voltage programming facilities to bring isotopes into resonance selectively with the tuneable laser operating in frequency locked mode.

CLAIMS

1. An instrument comprising a Plasma Source Mass Spectrometer equipped with dual ion detectors.

2. An instrument according to claim 1 which is an Inductively Coupled Plasma Mass Spectrometer.

3. An instrument according to claim 1 wherein ions transmitted by the mass spectrometer are detected with high selectivity and specificity *via.* optical spectroscopy.

4. An instrument according to claim 3 wherein the specific detection of the transmitted ions is *via* resonance scattering processes.

5. An instrument according to claim 4 wherein the specific detection of the transmitted ions is *via* laser induced fluorescence.

6. An instrument according to claim 4 provided with means for detecting resonantly scattered photons.

7. An instrument according to claim 6 provided with means for the detection of the resonantly scattered photons with high temporal and spatial resolution.

8. An instrument according to claim 7 wherein the detection of resonantly scattered photons is *via* an imaging photomultiplier tube.

9. An instrument according to claim 1 wherein the second detector is a non-specific ion counting device.

10. An instrument according to claim 9 wherein the non-specific ion counting device is an electron multiplier.

11. An instrument according to claim 1 wherein the dual ion detectors are correlated temporally with high resolution.

12. An instrument according to claim 11 wherein the dual ion detectors comprise a specific optical ion detector and a non-specific ion detector.

13. An instrument according to claim 11 that provides co-incidence detection of transmitted ions.

14. An instrument according to claim 1 wherein the ion beam energies may be manipulated to compress the optical bandwidth of the transmitted ions.

15. An instrument according to claim 14 provided with means for reducing the spread of the ion beams energies.

16. An instrument according to claim 15 wherein a front-end collision/reaction cell is used to reduce the spread of the ion beam energies.

17. An instrument according to claim 14 provided with means for accelerating the transmitted ion beam to raise the average ion beam energy.

18. An instrument according to claim 4 provided with means for manipulating the ion beam energies to bring the transmitted ion beam into resonance within the detection volume of the optical detector.

19. An instrument according to claim 18 provided with means for accelerating the ion beam.

20. An instrument according to claim 1 wherein the ion beam is accelerated to induce an optical isotope shift by Doppler shifting.

21. An instrument according to claim 1 wherein a multiple exit slit assembly is incorporated.

22. An instrument according to claim 21 wherein the dual detector assembly is mounted upon the multiple slit assembly

23. An instrument according to claim 22 wherein the dual detector assembly is mounted upon the axial exit slit.

24. An instrument according to claim 21 wherein additional non-specific ion detectors are mounted upon the multiple exit slit assembly.

25. An instrument according to claim 24 wherein additional non-specific ion detectors are mounted upon the off-axis exit slits.

26. An instrument according to claim 25 wherein the non-specific ion detectors are electron multiplier devices.

27. A method for detecting low concentrations of stable and/or radioisotopes and/or low abundance isotopes which comprises analysing a sample in an instrument according to claim 1.

28. A method according to Claim 27 wherein the species being detected is a radionuclide.

29. A method according to Claim 28 wherein the radionuclide is an actinide.

30. A method according to Claim 29 wherein the actinide is plutonium.

31. A method according to claim 27 wherein single photon detection, single colour, two-colour and multiphoton excitation, and combinations thereof, are employed to increase the range of ions that can be detected.

32. A method according to claim 27 wherein selectivity is enhanced by specific optical detection of transmitted ions.

33. A method according to claim 27 wherein selectivity is enhanced by specific isotopic selection via optical isotope shifts.

34. A method according to claim 27 wherein selectivity is enhanced by inducing an optical isotope shift by acceleration of the transmitted ions with subsequent Doppler shifting.

35. A method according to claim 27 wherein selectivity is enhanced by optical probing of hyperfine splitting.

36. A method according to claim 27 wherein non-specific background is reduced by co-incidence detection of transmitted ions with subsequent improved detection limit.

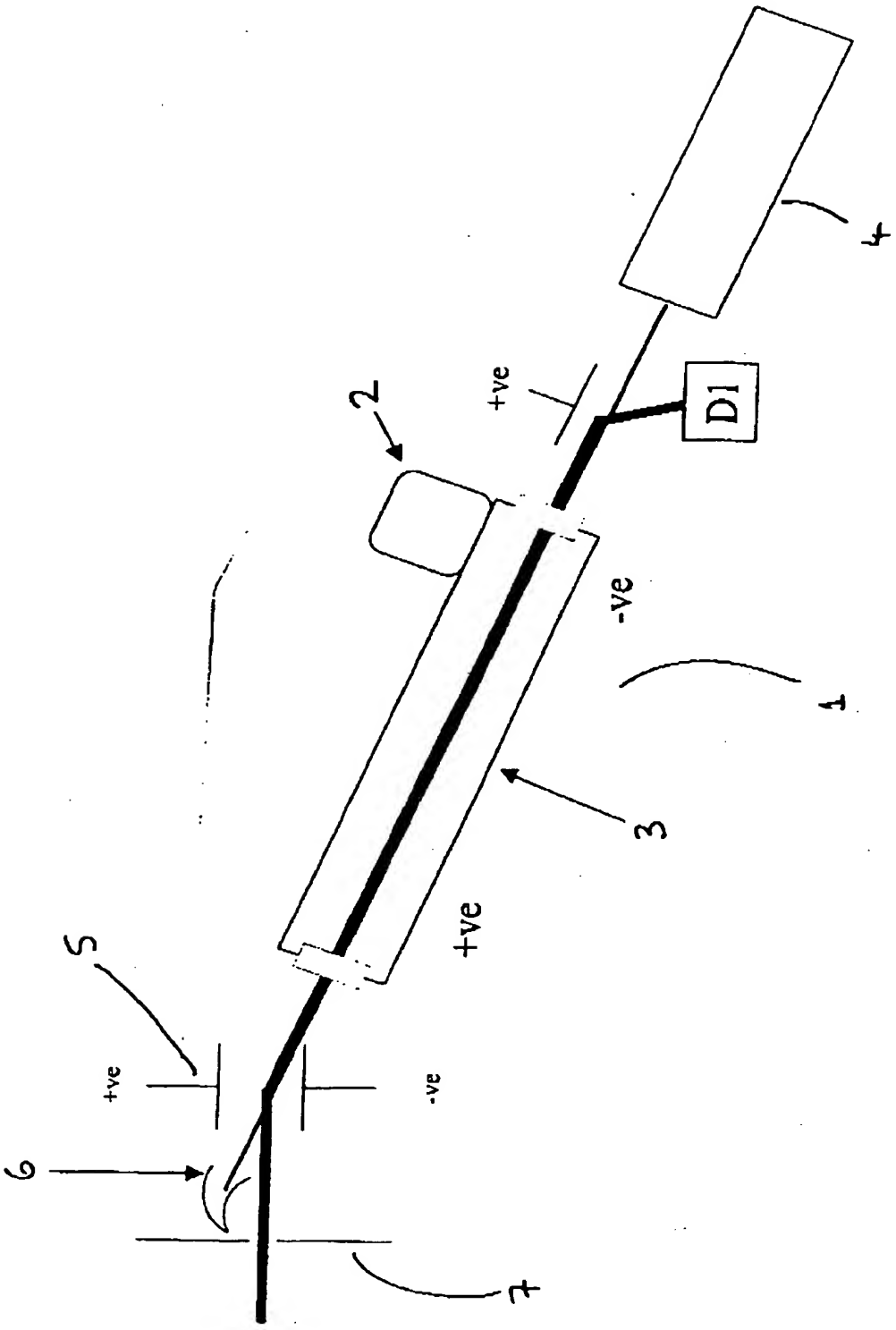

Fig 1

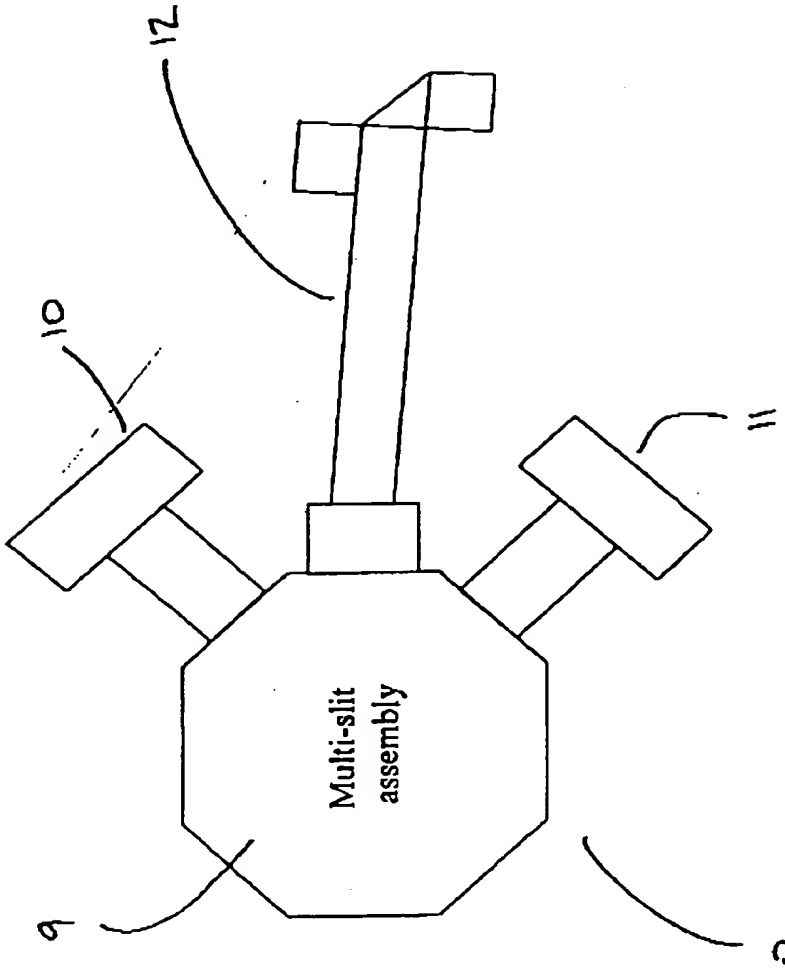

Fig. 2